

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 13/00	A1	(11) International Publication Number: WO 95/32927 (43) International Publication Date: 7 December 1995 (07.12.95)
(21) International Application Number: PCT/EP95/01993 (22) International Filing Date: 24 May 1995 (24.05.95) (30) Priority Data: P 44 18 726.2 28 May 1994 (28.05.94) DE (71) Applicant (for all designated States except US): ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR). (72) Inventors; and (75) Inventors/Applicants (for US only): DE MERINGO, Alain [FR/FR]; 294, rue Saint-Jacques, F-75005 Paris (FR). BATTIGELLI, Jean [FR/FR]; 17, rue E.-Vaillant, F- 60290 Rantigny (FR). FURTAK, Hans [DE/DE]; Im Oberkämmerer 35, D-67346 Speyer am Rhein (DE). (74) Agent: KADOR & PARTNER; Corneliusstrasse 15, D-80469 Munich (DE).		(81) Designated States: AU, BR, CA, CN, CZ, FI, HU, JP, KR, MX, NO, NZ, PL, SI, SK, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: GLASS-FIBER COMPOSITIONS (57) Abstract A biologically degradable glass-fiber composition characterized by the following constituents in percent by weight: SiO ₂ 45 to 60, Al ₂ O ₃ less than 2, CaO + MgO 10 to 16, Na ₂ O + K ₂ O 15 to 23, B ₂ O ₃ 10 to 18, P ₂ O ₅ 0 to 4, BaO 0 to 1, diverse 0 to 2.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Glass-fiber compositions

The present invention relates to a glass-fiber composition that is biologically degradable.

The prior art describes some glass-fiber compositions which are said to be biologically degradable.

The biological degradability of glass-fiber compositions is of great importance because various studies point out that some glass fibers with very small diameters in the range of less than 3 microns may be carcinogenic, while biologically degradable glass fibers of such dimensions show no carcinogenicity.

However not only the biological degradability is of crucial importance but also the mechanical and thermal properties of the glass fibers, or the products produced therefrom, the resistance of the glass fibers and the processibility of the glass-fiber composition. For example glass fibers are used to a great extent for insulation purposes. For these applications sufficient moisture-resistance is necessary.

Also, the glass-fiber composition must permit processibility by known methods for producing glass fibers with a small diameter, for example the centrifugal technique, in particular the inner centrifugal technique (this technique is described for example in US-PS 4 203 745).

The invention is based on the problem of providing a novel glass-fiber composition that is characterized by biological degradability, has good stability or resistance to moisture and is easy to process.

The invention is based on the finding that this problem can be solved by a glass-fiber composition that contains considerable amounts of alkali oxides and boron oxide, as well as optionally aluminum oxide.

It has turned out that such a glass-fiber composition fulfills the combination of the necessary properties, namely

biological degradability, resistance to moisture and good processibility.

The object of the invention is a glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
$\text{CaO} + \text{MgO}$	10 to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	15 to 23
B_2O_3	10 to 18
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

The inventive glass-fiber compositions are processible by the centrifugal technique. The obtained fibers have good resistance to moisture. Surprisingly enough, the glass-fiber compositions show biological degradability. The mean fiber diameter is preferably less than 10 microns and is in particular between 2.5 and 5 microns.

The inventive glass-fiber compositions preferably have the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
$\text{CaO} + \text{MgO}$	10 to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	more than 18
B_2O_3	less than 12
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

According to a further preferred embodiment the inventive glass-fiber compositions have the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
$\text{CaO} + \text{MgO}$	10 to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	less than 18
B_2O_3	more than 12
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

The inventive glass-fiber compositions preferably have less than 57 percent by weight silicon dioxide, in particular less than 56.5 percent by weight.

By adding aluminum oxide one can obtain an improvement in moisture-resistance. The inventive compositions are therefore preferably given at least 0.1 percent by weight, in particular at least 0.5 percent by weight, and usually less than 1.5 percent by weight aluminum oxide.

Biological degradability can be increased by the addition of phosphorus pentoxide. The inventive compositions therefore preferably contain at least 0.1 percent by weight P_2O_5 .

According to a further preferred embodiment the composition contains less than 2 percent by weight magnesium oxide.

The moisture-resistance of the inventive glass-fiber compositions was determined by a standard method known as the DGG method. In the DGG method 10 g finely ground glass with a grain size between about 360 and 400 microns is held at the boiling point for five hours in 100 ml water. After quick cooling of the material the solution is filtered and a certain volume of the filtrate evaporated to dryness. The weight of the thus obtained dry material permits the amount of glass dissolved in the water to be calculated. The amount is stated in milligrams per gram of tested glass.

The biological degradability of the inventive glass compositions was tested by introducing 1 g of the glass

powder, as described for the DGG method, into a physiological solution with the composition stated below and a pH value of 7.4:

NaCl	6.78
NH ₄ Cl	0.535
NaHCO ₃	2.268
NaH ₂ PO ₄ ·H ₂ O	0.166
(Na ₃ citrate)·2H ₂ O	0.059
Glycine	0.450
H ₂ SO ₄	0.049
CaCl ₂	0.022

Dynamic test conditions were selected as are described in Scholze and Conradt. The flow rate was 300 ml/day. The duration of the test was 14 days. The results are stated as percent of SiO₂ in the solution x 100 after 14 days.

The invention shall be described in more detail in the following with reference to examples.

Example 1

A glass of the following composition in percent by weight was melted:

SiO ₂	56.0
Al ₂ O ₃	1.0
CaO	9.0
MgO	4.0
Na ₂ O	18.0
K ₂ O	1.0
B ₂ O ₃	10.5
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 mg/g was determined.

The above-described test for biological degradability yielded a value of 550.

Example 2

A glass with the following composition in percent by weight was melted:

SiO ₂	55.0
Al ₂ O ₃	1.0
CaO	9.0
MgO	4.0
Na ₂ O	18.0
K ₂ O	1.0
B ₂ O ₃	10.5
P ₂ O ₅	1.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 3

A glass with the following composition in percent by weight was melted:

SiO ₂	57.5
Al ₂ O ₃	0.5
CaO	8.0
MgO	3.5
Na ₂ O	17.8
K ₂ O	0.2
B ₂ O ₃	12.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 50 mg/g was determined.

The above-described test for biological degradability yielded a value of 550.

Example 4

A glass with the following composition in percent by weight was melted:

SiO ₂	56.5
Al ₂ O ₃	0.5
CaO	8.0
MgO	3.5
Na ₂ O	17.8
K ₂ O	0.2
B ₂ O ₃	12.0
P ₂ O ₅	1.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 50 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 5

A glass with the following composition in percent by weight was melted:

SiO ₂	57.5
Al ₂ O ₃	0.5
CaO	8.1
MgO	3.6
Na ₂ O	17.25
K ₂ O	0.35
B ₂ O ₃	12.4
Diverse	0.3.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 6

A glass with the following composition in percent by weight was melted:

SiO ₂	57.5
Al ₂ O ₃	0.5
CaO	8.3
MgO	1.8
Na ₂ O	18.6
K ₂ O	0.4

B_2O_3	11.5
BaO	1.0
Diverse	0.4.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 7

A glass with the following composition in percent by weight was melted:

SiO_2	57.5
Al_2O_3	0.5
CaO	8.3
MgO	1.8
Na_2O	17.1
K_2O	0.4
B_2O_3	13.0
BaO	1.0
Diverse	0.4.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 8

A glass with the following composition in percent by weight was melted:

SiO_2	57.5
Al_2O_3	0.5
CaO	8.4
MgO	1.7
Na_2O	17.0
K_2O	0.5
B_2O_3	14.0
Diverse	0.4.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Claims

1. A glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	45	to	60
Al_2O_3	less	than	2
$\text{CaO} + \text{MgO}$	10	to	16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	15	to	23
B_2O_3	10	to	18
P_2O_5	0	to	4
BaO	0	to	1
Diverse	0	to	2.

2. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	45	to	60
Al_2O_3	less	than	2
$\text{CaO} + \text{MgO}$	10	to	16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	more	than	18
B_2O_3	less	than	12
P_2O_5	0	to	4
BaO	0	to	1
Diverse	0	to	2.

3. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	45	to	60
Al_2O_3	less	than	2
$\text{CaO} + \text{MgO}$	10	to	16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	less	than	18
B_2O_3	more	than	12
P_2O_5	0	to	4

BaO	0	to	1
Diverse	0	to	2.

4. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO ₂	47	to	57
Al ₂ O ₃	less	than	2
CaO + MgO	12	to	15
Na ₂ O + K ₂ O	16	to	20
B ₂ O ₃	10	to	16
P ₂ O ₅	0	to	2
BaO	0	to	1
Diverse	0	to	2.

5. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO ₂	52	to	60
Al ₂ O ₃	0	to	1.5
CaO + MgO	11	to	12.5
Na ₂ O + K ₂ O	16	to	18.5
B ₂ O ₃	10	to	14
P ₂ O ₅	0	to	1
BaO	0	to	1
Diverse	0	to	2.

6. The glass-fiber composition of any of claims 1 to 5, characterized in that the content of silicon dioxide is less than 57 percent by weight.

7. The glass-fiber composition of any of claims 1 to 6, characterized in that the content of silicon dioxide is less than 56.5 percent by weight.

8. The glass-fiber composition of any of claims 1 to 7, characterized in that the content of aluminum oxide is at least 0.1 percent by weight.

9. The glass-fiber composition of any of claims 1 to 8, characterized in that the content of aluminum oxide is at least 0.5 percent by weight.

10. The glass-fiber composition of any of claims 1 to 9, characterized in that the content of phosphorus oxide is at least 0.1 percent by weight.

11. The glass-fiber composition of any of claims 1 to 10, characterized in that the content of boron oxide is more than 12 percent by weight.

12. The glass-fiber composition of any of claims 1 to 11, characterized in that the content of magnesium oxide is less than 2 percent by weight.

INTERNATIONAL SEARCH REPORT

national Application No
PCT/EP 95/01993

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 412 878 (ISOVER SAINT-GOBAIN) 13 February 1991 see claims; example 11 ---	1,5, 8-10,12
A	US,A,5 055 428 (PORTER) 8 October 1991 see the whole document ---	1-12
A	GB,A,1 096 465 (UNITED STATES GYPSUM COMPANY) 29 December 1967 see claims; examples ---	1-12
A	EP,A,0 588 251 (SCHULLER INTERNATIONAL, INC.) 23 March 1994 see claims 1-3; tables 1,2 ---	1-12
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

Date of the actual completion of the international search

10 August 1995

Date of mailing of the international search report

31.08.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Van Bommel, L

INTERNATIONAL SEARCH REPORT

I. International Application No
PCT/EP 95/01993

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GLASTECHNISCHE BERICHTE, vol. 64, no. 1, January 1991 FRANKFURT DE, pages 16-28, XP 000178832 R. M. POTTER ET AL. 'Glass Fiber dissolution in a Physiological Saline Solution' see page 26 - page 27; table 2 -----</p>	1

INTERNATIONAL SEARCH REPORT

national Application No
PCT/EP 95/01993

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-412878	13-02-91	FR-A- 2650821	15-02-91
		FR-A- 2658182	16-08-91
		AU-B- 630484	29-10-92
		AU-A- 6002590	14-02-91
		CA-A- 2022446	12-02-91
		CN-A,B 1049834	13-03-91
		CN-A- 1093066	05-10-94
		DE-D- 69007369	21-04-94
		DE-T- 69007369	13-10-94
		ES-T- 2053139	16-07-94
		HU-B- 210633	28-06-95
		JP-A- 3093650	18-04-91
		PL-B- 165859	28-02-95
		SI-A- 9011548	31-12-94
		US-A- 5108957	28-04-92
		US-A- 5250488	05-10-93
US-A-5055428	08-10-91	AU-A- 8625091	15-04-92
		DE-D- 69109083	24-05-95
		EP-A- 0502159	09-09-92
		ES-T- 2072016	01-07-95
		JP-T- 5502432	28-04-93
		WO-A- 9205121	02-04-92
GB-A-1096465		BE-A- 657609	16-04-65
		CH-A- 499466	30-11-70
		DE-A- 1496679	29-05-69
		FR-A- 1421742	09-03-66
		LU-A- 47644	23-02-65
		NL-A- 6415101	28-06-65
		US-A- 3294505	27-12-66
EP-A-588251	23-03-94	US-A- 5401693	28-03-95
		CA-A- 2106412	19-03-94
		JP-A- 6321578	22-11-94